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1,3-DIISONITROSOACETONE AND 4,4′–BIS(DIETHYLAMINO)BENZOPHENONE OXIME AS METHANESULFONYL CHLORIDE VAPOR-SENSING COATINGS FOR OPTICAL-BASED MICROSENSORS

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The chromogenic detector reagents 1,3-diisonitrosoacetone (DIA) and 4,4'-bis(diethylamino)benzophenone oxime (EMKO) have been studied as solid-state coatings for sensing methane-sulfonyl chloride vapor. The strength of the optical detection signals produced on contact of the coatings with methanesulfonyl chloride vapor are strongly affected by the composition of the solid reaction support; silica gel is the preferred support for coatings made with either reagent. When monitored with a fiber-optic spectrophotometer, coatings made with DIA and EMKO are capable of sensing methanesulfonyl chloride vapor down to the low parts per million level. At 25 °C, the DIA coatings are stable for up to 5 days while the EMKO coatings are stable for <1 day.

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4,4'-Bis(diethylamino)benzophenone oxime,
Microsensor coating, Chromogenic, ~~EMKO~~
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PREFACE

The work described in this report was authorized under Project No. 1C162706A553, CB Defense and General Investigation. This work was started in November 1986 and completed in October 1987. It is reported in laboratory notebooks 86-0006, 86-0209, and 87-0019.

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1,3-DIISONITROSOACETONE AND 4,4'-BIS(DIETHYLAMINO)BENZOPHENONE OXIME AS METHANESULFONYL CHLORIDE VAPOR-SENSING COATINGS FOR OPTICAL-BASED MICROSENSORS

1. INTRODUCTION

Currently, there is interest in developing small, lightweight, portable devices for sensing minute quantities of chemical agent vapors. Fiber-optic waveguides recently adapted for use in chemical analyses[1] or similar types of optical-detection devices using vapor-sensing coatings may ultimately be developed as microsensors to satisfy this need.

Vapor-sensing coating materials for the optical-based microsensors can be chromogenic detector reagents of the "direct-acting" type; that is, they change color when they come in contact with the analyte. Two direct-acting chromogenic reagents are of special interest as candidate microsensor coatings because of their reported capability of detecting nerve agents at low vapor concentration levels. A crayon containing 1,3-diisonitrosoacetone (DIA) was reported[2] to be capable of detecting the nerve agent GB (isopropyl methylphosphonofluoridate) in air at a concentration of 1 µg/L (ca. 0.2 ppm) after a 6-min exposure. A similar composition containing 4,4'-bis(diethylamino)benzophenone oxime, also known as Ethyl Michler's Ketone Oxime (EMKO), was reported[3] to be capable of detecting the nerve agent GA (ethyl dimethylphosphoroamidocyanate) in air at a concentration of 44 µg/L (ca. 6 ppm) in <10 s. Mechanisms of the reactions of DIA[4] and EMKO[5] that lead to the formation of colored products have also been reported. We report here results of studies that were carried out with methanesulfonyl chloride (MSC), a nerve agent simulant, to determine spectral properties of sensitive solid-state coatings made with DIA and EMKO for a starting point in studies with nerve agents and to identify essential characteristics of detection hardware that can use the coatings.

2. EXPERIMENTAL PROCEDURES

2.1 Materials.

1,3-Diisonitrosoacetone guanidinium salt was obtained from Polysciences, Inc. (Warrington, PA) and 4,4'-bis(diethylamino)benzophenone oxime was obtained from a custom synthesis carried out by HJ Laboratories (Columbus, OH). Methanesulfonyl chloride was obtained from Aldrich Chemical Company (Milwaukee, WI). Media (tlc) containing silica gel (Type 5539) and cellulose (Type 5552-7) were obtained from E. Merck AG [Darmstadt, Germany, E.M. Science (Cherry Hill, NJ)]. Alumina tlc media (Type 060408) was obtained from Fluka Chemical Corporation (Ronkonkoma, NY). Glass fiber support material (Type 8064) was obtained from Gelman, Inc. (Ann Arbor, MI).

2.2 Equipment and Procedures.

2.2.1 Preparation of Coatings.

The DIA and EMKO reagents were tested after they had been applied to solid supports. The DIA salt (10 mg/mL) was dissolved in water, an' EMKO

(75 mg/mL) was dissolved in dichloromethane. Supports were coated by adding a 4-µL drop of solution containing the candidate reagent to a piece of the support (1/2 by 1/2 in.) and allowing the solvent to evaporate.

2.2.2 Gas-Solid Reaction Studies.

A sketch of the apparatus used for the gas-solid reaction studies that includes a chemical vapor generator, a Teflon reaction chamber, and a fiber-optic spectrophotometer is shown in Figure 1. The chemical vapor generator[6] supplied the required levels of MSC vapor. The gas-solid reaction involving the candidate coating and test vapor was carried out in the reaction chamber, and the color change that occurred in the coating was monitored with the fiber-optic spectrophotometer.

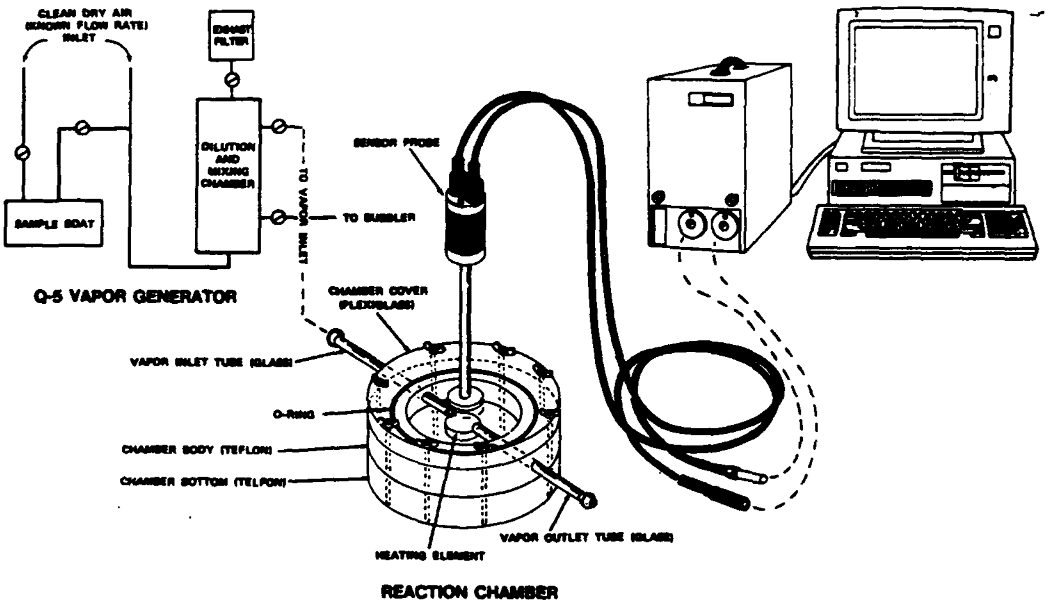

Figure 1. Apparatus for Gas-Solid Reaction Studies

The fiber-optic spectrophotometer (an Optical Waveguide Spectrum Analyzer Model 200) was from Guided Wave, Incorporated (Rancho Cordova, CA).[7] A silicon detector and a six-to-one probe (Catalog No. WW100-1) were used. The reflectance tip was removed from the probe, and the end of the probe was positioned so that it was 5 mm directly above the portion of a solid support that contained the candidate coating. The probe was clamped, keeping it perpendicular to the surface of the solid support. Reflectance spectra of the coating were obtained by positioning the probe in this manner.

The required level of MSC vapor was obtained by regulating the flow rates of the vapor and dilution streams in the chemical vapor generator. Collecting the vapor in 2-methoxyethanol and assaying the solution spectrophotometrically at 510 nm using EMKO as the analytical reagent determined actual MSC concentrations.

The coated support was placed coated side up on the top surface of a metal heating element in the reaction chamber. The support was positioned so the coating was directly below the fiber-optic probe. The tests were carried out at room temperature (25-28 °C). Prior to an experiment, the fiber-optic spectrophotometer was adjusted to perform optimally, and the vapor generator was adjusted so the required concentration of MSC vapor was being generated. The vapor stream was vented until a reference spectrum of the coating was obtained. After the reference spectrum was obtained, the inlet and outlet valves of the reaction chamber were set so MSC vapor passed through the chamber. Reflectance spectra covering a preselected spectral region were then obtained with time.

2.2.3 Stability Studies.

Exposing coatings that had been aged at 25 °C to MSC vapor (ca. 4000 ppm) and visually determining when the extent of aging affected the chromogenic response determined the stability of the coatings on silica gel supports. A typical test was performed as follows. A piece of the aged coated support (1/2 by 1/2 in.) was attached to a microscope slide with cellophane tape. When the support was attached to the slide, care was taken to see that the coating was not covered. The slide was placed in a 250-cm^3 jar so the top of the slide rested against the wall. Using a 10-μL syringe, a solution of MSC in dichloromethane (10 μL, 10% v/v) was injected along the inside wall of the jar. The jar was capped, and the coating was visually observed to determine the time required to produce a color change.

3. RESULTS AND DISCUSSION

Tests conducted by exposing a DIA or EMKO coating on four different types of solid supports to MSC vapor (20 ppm) showed that silica gel is the preferred reaction support (Figures 2 and 3). Each bar in the graphs represents the difference in the signal intensity obtained before and after exposure to MSC vapor. Compared with the next best support for each coating, the responses of the DIA and EMKO reagents coated on the silica gel support were about 10 times and 6 times as large, respectively. Consequently, silica gel was selected as the reaction support for the coatings that were studied in detail.

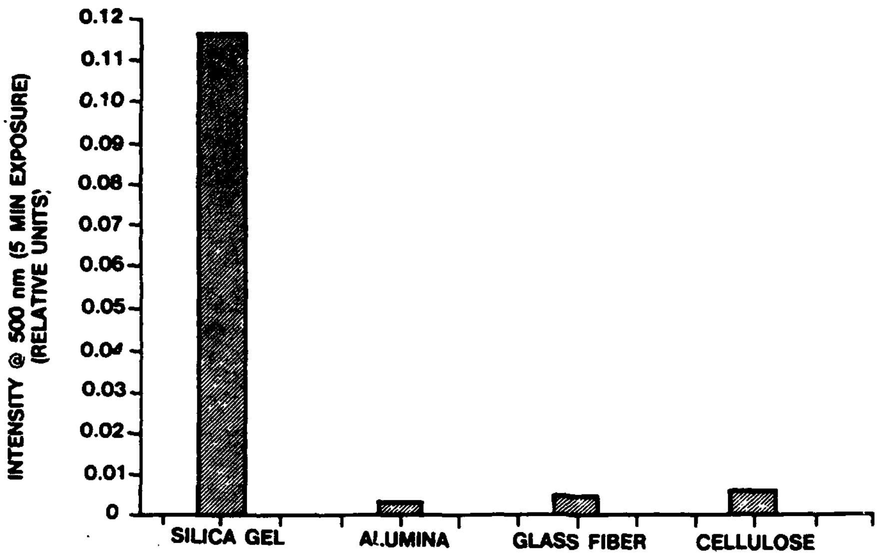

Figure 2. Effect of Composition of Solid Support on the Response of DIA Coatings Exposed to MSC Vapor

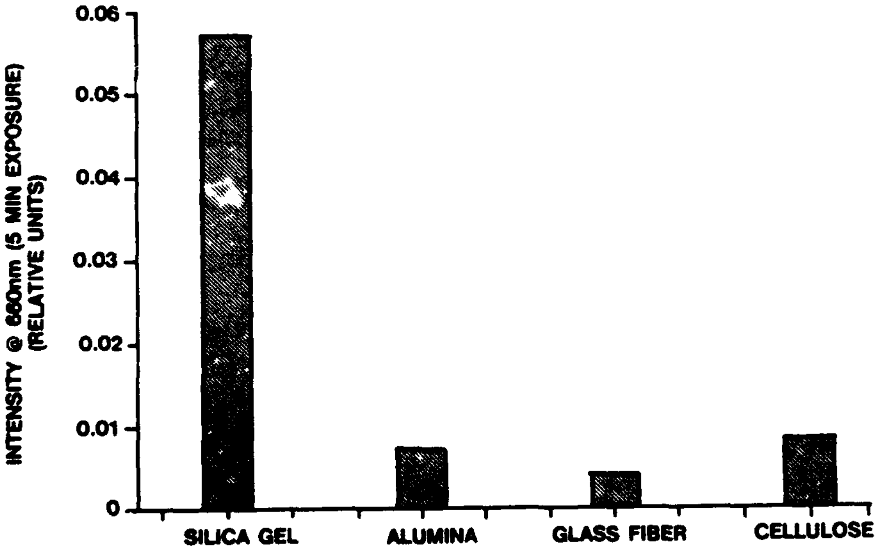

Figure 3. Effect of Composition of Solid Support on the Response of EMKO Coatings Exposed to MSC Vapor

Figures 4 and 5 contain the reflectance spectra obtained with time during the reactions of MSC vapor with DIA and EMKO coatings, respectively. The MSC vapor concentrations were 14 ppm for studies with DIA and 18.5 ppm for studies with EMKO. The DIA coating produced a single broad peak in the visible region of the spectrum with a reflectance maximum at 500 nm. The EMKO coating also produced a reflectance maximum near 500 nm but differed from the response of the DIA coating in that it also produced prominent shoulders near 550 and 660 nm.

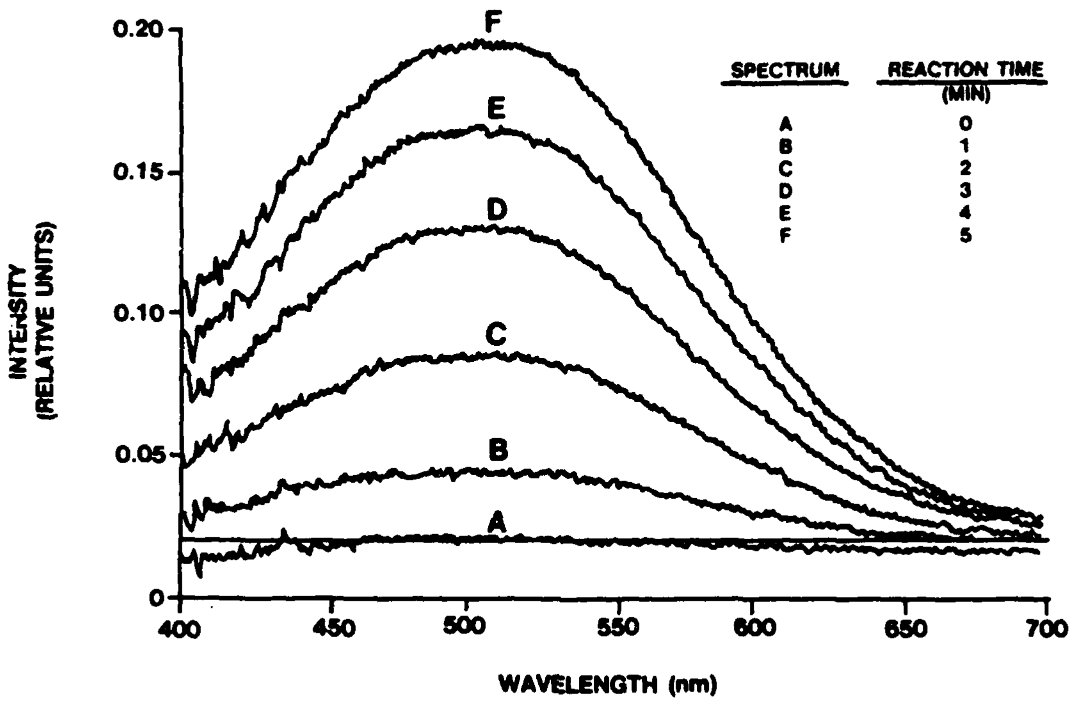

Figure 4. Spectra from Reaction of DIA Coating on Silica Gel Support with MSC Vapor as a Function of Time

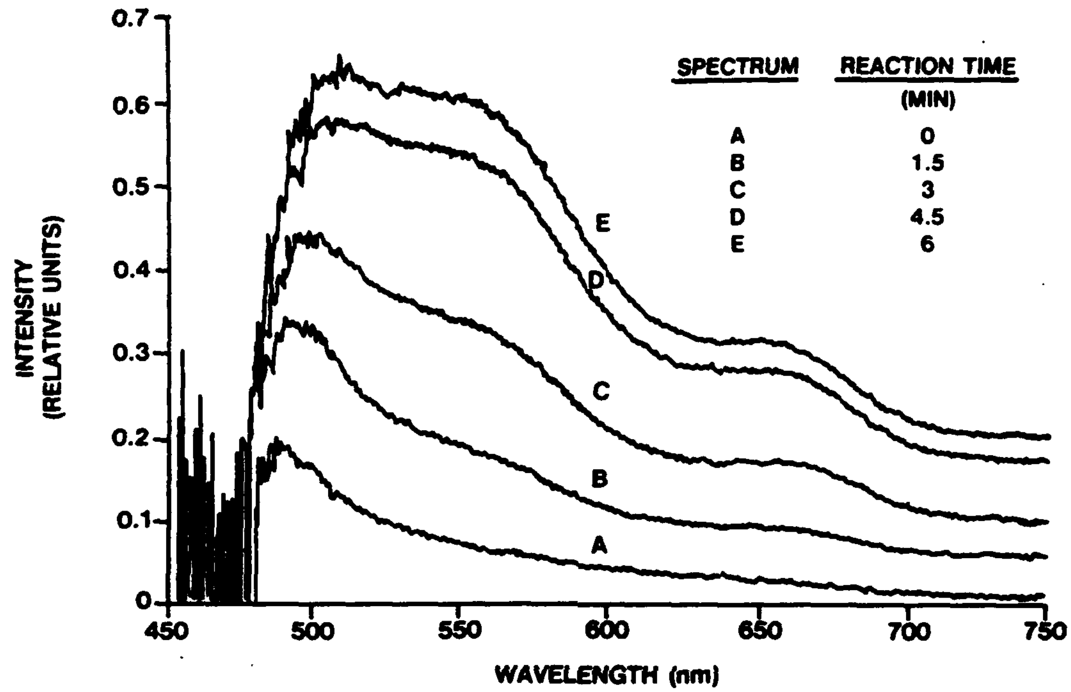

Figure 5. Spectra from Reaction of EMKO Coating on Silica Gel Support with MSC Vapor as a Function of Time.

The spectra of the DIA coating did not differ from that of the background (silica gel support) until it was exposed to MSC vapor; hence, the optimum wavelength for monitoring the coating is 500 nm, which is the reflectance maximum of the colored product. With EMKO, the optimum wavelength was more difficult to ascertain, because the coating degraded when it was illuminated with light from the fiber-optic probe. Reflectance spectra obtained as a function of time for the EMKO coating illuminated with light from the fiber-optic probe in the absence of MSC vapor are shown in Figure 6. The strongest increase in the intensity of reflectance occurred in the 450-550-nm range; but some increase occurred even up to 700 nm. Because the change in reflectance due to photodegradation of the coating was smallest in the higher wavelength region of the spectrum, 660 nm was judged to be the optimum wavelength to monitor the EMKO coating.

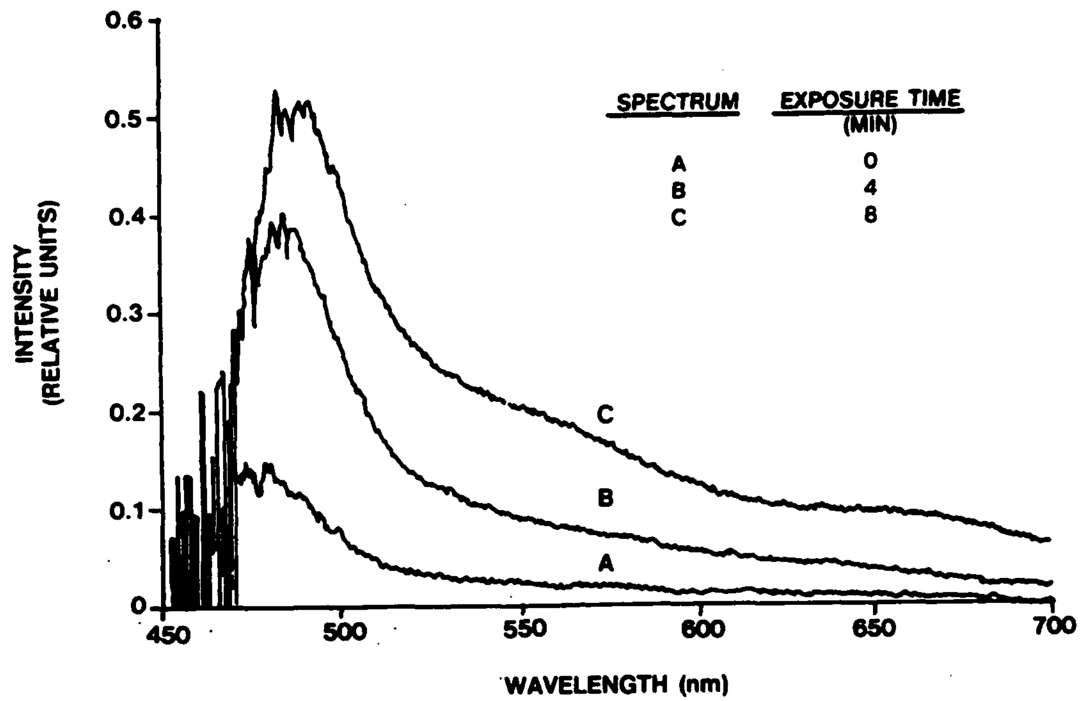

Figure 6. Spectra Showing Effect of Photochemical Decomposition of EMKO Coated on a Silica Gel Support as a Function of Time

After the optimum wavelengths for monitoring the responses of the coatings had been selected, detection profiles for the coatings in the presence of various concentrations of MSC vapor were determined. These results are shown for the DIA coating in Figure 7 and for the EMKO coating in Figure 8. The data in these figures indicate that both the DIA and EMKO coatings are capable of detecting MSC vapors in the low parts per million (ppm) range. However, the DIA coating has a significant advantage over the EMKO coating, because it gives a sharper change in the detection profile when the coating initially comes in contact with MSC vapor and the baseline (region of detection profile obtained prior to exposure to MSC vapor) contains much less noise. Thus, a lower detection limit for MSC and other analytes will probably be attainable with the DIA coating.

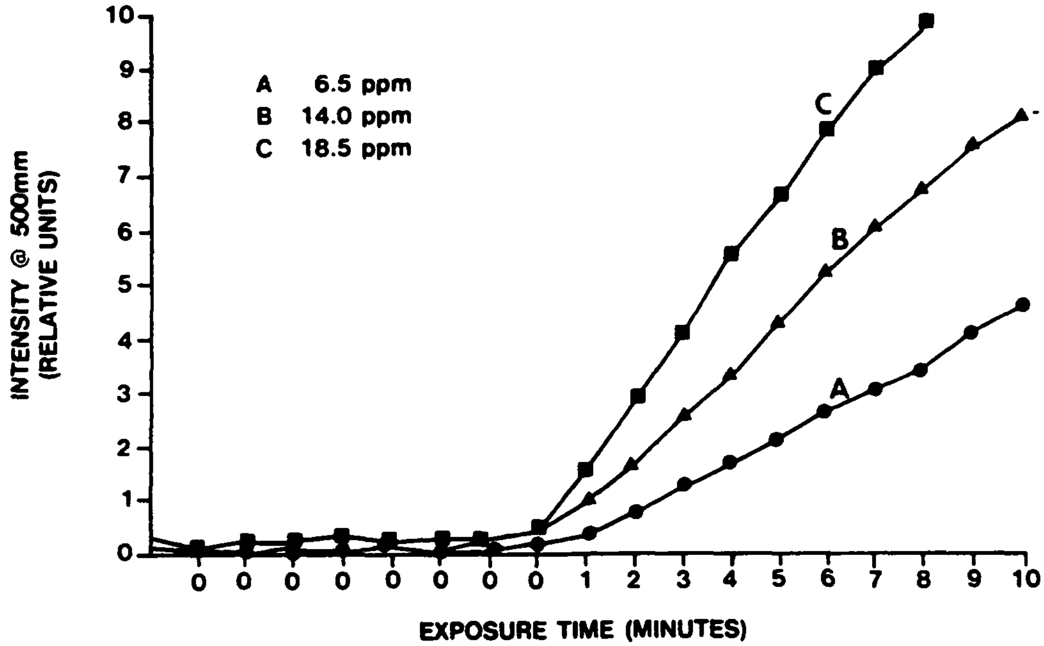

Figure 7. Detection Profiles for Reaction of DIA Coating with Three Different Levels of MSC Vapor

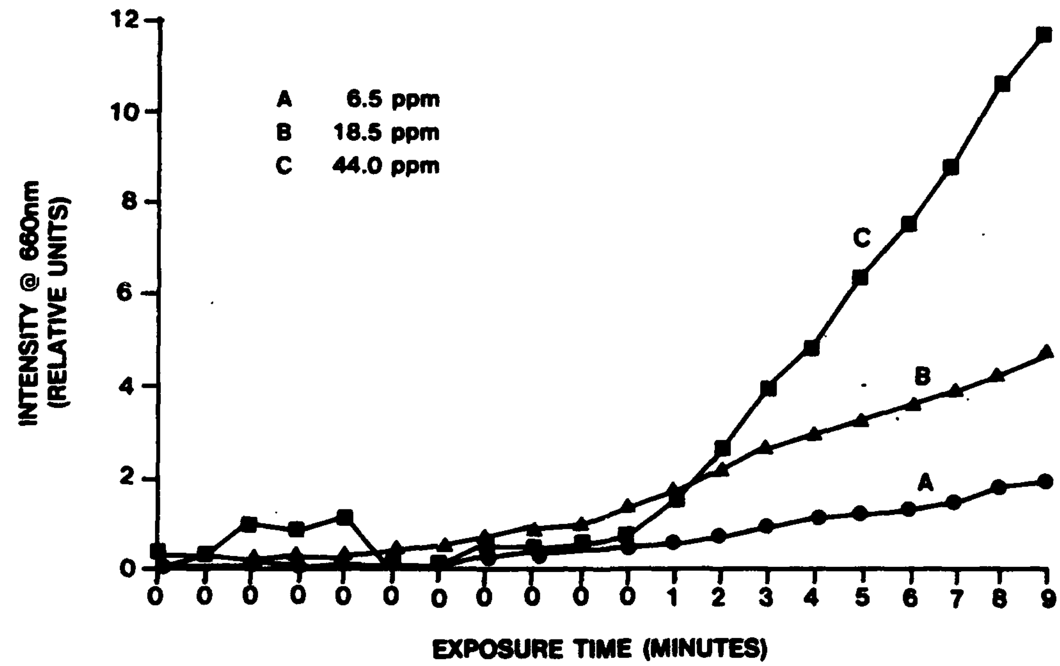

Figure 8. Detection Profiles for Reaction of EMKO Coating with Three Different Levels of MSC Vapor

The table contains results of stability studies carried out by visually monitoring the responses to MSC vapor (ca. 4000 ppm) of DIA and EMKO coatings that had been stored in the dark at 25 °C.

Table. Stability Studies of DIA and EMKO Coatings

COATING	AGING TIME (days)	DETECTION RESPONSE (color change; response time)
DIA	0-5	colorless-->magenta; 45 s
	6	colorless-->magenta; 1 min
EMKO	0	bright yellow-->red; 3.5 min
	1	bright yellow-->red; 4 min
	2	dark yellow-->red; 15 min
	3	yellow brown-->red; 15 min

No change was observed in the response of DIA coatings stored up to 5 days in the dark. By comparison, EMKO coatings showed some deterioration in response time after being stored only 1 day and pronounced deterioration in the time and quality of the visual response after having been stored 2 days. In tests conducted with coatings that had been stored under fluorescent illumination (430 lx), DIA coatings performed the same as those aged in dark; whereas, EMKO coatings stored for less than 10 min showed significant degradation.

4. CONCLUSIONS

This study shows that the strength of the response of DIA and EMKO coatings to MSC vapor are strongly affected by the composition of the solid reaction support. Based on the strength of the detection signal produced during exposure of the coatings to MSC vapor, silica gel is the preferred support for coatings made with either reagent. Coatings made with DIA or EMKO are capable of sensing MSC vapor down to the low ppm level. However, only the DIA coating has sufficient stability (5 days at 25 °C) for use as a vapor-sensing coating for solid-state sensors. Because of the limited stability of the DIA reagent, provisions should be included in the design of the detection hardware to enable frequent replacement of the coated support. Also, the hardware should include provisions for monitoring the DIA coating at 500 nm.

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